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(19) (CA) **CANADIAN PATENT** (12)

(54) Removal of CO<sub>2</sub> and/or H<sub>2</sub>S from Gases

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Abstract of the Disclosure:  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  are removed from gases which contain  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  by means of an aqueous alkanolamine-containing absorption liquid, by a process in which the said gas is treated, in an absorption stage, at from 40 to 100°C, with an aqueous absorption liquid containing from 20 to 70% by weight of methyl-diethanolamine, the treated gas is taken off at the top of the absorption stage, the aqueous absorption liquid laden with  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  is removed at the bottom of the absorption stage and is regenerated by being let down in two or more flash stages, the final flash stage being operated under reduced pressure and the latter being generated by means of a mechanical apparatus for producing reduced pressure and a steam-jet ejector, which are connected in series, and the regenerated absorption liquid is recycled to the absorption stage.

Removal of CO<sub>2</sub> and/or H<sub>2</sub>S from gases

The present invention relates to a process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from gases by means of an aqueous absorption liquid.

5 It has been disclosed, for example by A.L. Kohl and F.C. Riesenfeld in Gas Purification, 3rd edition, 1979, that aqueous solutions of monoethanolamine or diethanolamine or mixtures of cyclotetramethylene sulfone and an aqueous solution of diisopropanolamine can be used  
10 as solvents for removing CO<sub>2</sub> and/or H<sub>2</sub>S from gases. In these processes, the solvent laden with CO<sub>2</sub> and, where relevant, H<sub>2</sub>S has to be regenerated in a stripping column by feeding in steam, and this involves the consumption of a considerable amount of energy. In the removal of  
15 CO<sub>2</sub> and, if necessary, H<sub>2</sub>S from natural gases containing higher hydrocarbons by means of a mixture of cyclotetramethylene sulfone and an aqueous solution of diisopropanolamine, there is the additional disadvantage that the higher hydrocarbons have a relatively high solubility  
20 in this solvent, so that the acidic gas taken off at the top of the stripping column has a relatively high content of hydrocarbons, which, where the acidic gas contains H<sub>2</sub>S, can lead to difficulties in a downstream Claus plant. Moreover, primary or secondary alkanolamines,  
25 such as monoethanolamine or diethanolamine, can as a rule only be used as aqueous solutions having a relatively low concentration of these alkanolamines, since the use of higher concentrations may cause severe corrosion damage to parts of the plant.

30 There was therefore a need for a process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from gases, in which the disadvantages of the conventional processes can be avoided.

It is an object of the present invention to provide a process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from gases,  
35 in which both capital costs and energy costs can be reduced compared with the conventional processes.

We have found that this and other objects and



advantages are achieved, in accordance with the invention, by a process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from a gas containing CO<sub>2</sub> and/or H<sub>2</sub>S by means of an aqueous alkanolamine-containing absorption liquid, wherein, in an absorption stage, the gas containing CO<sub>2</sub> and/or H<sub>2</sub>S is treated at from 40 to 100°C with an aqueous absorption liquid which contains from 20 to 70 % by weight of methyl-diethanolamine, the treated gas is taken off at the top of the absorption stage, the aqueous absorption liquid laden with CO<sub>2</sub> and/or H<sub>2</sub>S is removed at the bottom of this stage and is regenerated by being let down in two or more flash stages, the final flash stage being operated under reduced pressure and the latter being generated by means of a mechanical apparatus for producing reduced pressure and a steam-jet ejector, which are connected in series, and the regenerated absorption liquid is recycled to the absorption stage.

In an advantageous embodiment of the process, the water losses resulting from removal of water in the gas streams taken off at the top of the absorption stage and from the flash stages are compensated by feeding in, at the bottom of the penultimate flash stage, an amount of steam corresponding to the water loss.

In the novel process, the solvent laden with CO<sub>2</sub> and/or H<sub>2</sub>S is regenerated solely by flashing, without the use of a stripping column, so that a substantial reduction in both capital costs and energy costs is achieved.

Furthermore, the novel process permits the use of a relatively high concentration of methyldiethanolamine in the absorption liquid, without resulting in corrosion damage in the gas washer. Another advantage of the process is that the water balance of the gas washer can be controlled in a simple manner. Using this procedure, it is possible to regulate not only the water balance of the gas washer but also its heat balance, so that any heat exchanger present in the gas washer for regulating the heat balance can be smaller or, if appropriate, can be omitted. The

procedure according to the invention gives a regenerated absorption liquid which has a low CO<sub>2</sub> and/or H<sub>2</sub>S content, so that it is possible to circulate smaller amounts of absorption liquid; this results in a corresponding saving of energy.

In another preferred embodiment of the process, the steam-jet ejector is downstream of the mechanical apparatus for generating reduced pressure. It may be advantageous if the gas taken off at the top of the final flash stage is fed in, together with the steam used to operate the steam-jet ejector, at the bottom of the penultimate flash stage.

Examples of gases which can be treated using the novel process are coal gasification gases, synthesis gases, coke oven gases and, preferably, natural gases. The process is advantageously used for removing CO<sub>2</sub> and/or H<sub>2</sub>S from natural gases which contain higher hydrocarbons in addition to methane. These higher hydrocarbons are in general C<sub>2</sub>-C<sub>30</sub>-hydrocarbons, in particular C<sub>2</sub>-C<sub>12</sub>-hydrocarbons, which as a rule are aliphatic, eg. ethane, propane, isobutane, n-butane, isopentane, n-pentane, the hexanes, heptanes, octanes, nonanes and decanes and the higher homologs. The higher hydrocarbons can contain, in addition to the aliphatic hydrocarbons, aromatic hydrocarbons such as benzene. In general, the natural gases contain from 0.1 to 40, preferably from 0.5 to 30, in particular from 1 to 20, mol % of the higher hydrocarbons.

The gases contain in general from 1 to 90, preferably from 2 to 90, in particular from 5 to 60, mol % of CO<sub>2</sub>. They can also contain H<sub>2</sub>S as a further acidic gas, or can contain H<sub>2</sub>S alone, for example in an amount from a few mol ppm, for example 1 mol ppm, to 50 mol %, preferably from 10 mol ppm to 40 mol %.

The solvent used for the novel process is an aqueous absorption liquid which contains from 20 to 70, preferably from 30 to 65, in particular from 40 to 60, % by weight of methyldiethanolamine. An aqueous methyldiethanolamine solution is advantageously employed, for

example an aqueous solution of technical-grade methyl-diethanolamine. In an advantageous embodiment of the process, an aqueous methyldiethanolamine solution which additionally contains from 0.05 to 1, in particular from 0.1 to 0.8, in particular from 0.1 to 0.6, mole/liter of a primary amine or alkanolamine, such as monoethanolamine, or preferably a secondary amine or alkanolamine, advantageously methylmonoethanolamine, very particularly advantageously piperazine, is used.

10 The aqueous absorption liquid containing from 20 to 70% by weight of methyldiethanolamine may additionally contain a physical solvent. Suitable physical solvents are, for example, N-methylpyrrolidone, tetramethylene sulfone, methanol and oligoethylene glycol dialkyl ethers, 15 such as oligoethylene glycol methyl isopropyl ether (SEPASOLV MPE)\* or oligoethylene glycol dimethyl ether (SELEXOL)\*. The physical solvent is present in the absorption liquid in general in an amount of from 1 to 60, preferably from 10 to 50, in particular from 20 to 40, % by 20 weight.

The novel process is carried out as follows: the gas containing CO<sub>2</sub> and/or H<sub>2</sub>S is first treated, in an absorption stage, with the methyldiethanolamine-containing absorption liquid. During this procedure, the temperature 25 of the absorption liquid in the absorption stage is maintained at from 40 to 100°C, preferably from 50 to 90°C, in particular from 60 to 80°C. In general, the pressure used in the absorption stage is from 10 to 110 bar. The absorption stage is advantageously an absorption column, 30 in general a packed column or a column equipped with trays. Advantageously, the gas to be treated is fed in at the bottom and the absorption liquid is fed in at the top of the absorption column, the acidic gases CO<sub>2</sub> and/or H<sub>2</sub>S being washed out by a countercurrent procedure. While any 35 H<sub>2</sub>S present is advantageously washed out to a substantial extent, in general so that the treated gas has an H<sub>2</sub>S content of not more than 120, preferably not more than 10,

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in particular not more than 3, mol ppm, it may be advantageous to wash out the CO<sub>2</sub> from the gas so that the treated gas contains not more than about 0.5 - 6, preferably from 0.5 to 5, in particular from 1 to 4, mol % of CO<sub>2</sub>. The

5 treated gas is advantageously taken off at the top of the absorption stage, expediently at a point above the feed of the absorption liquid. The absorption liquid laden with the acidic gases CO<sub>2</sub> and/or H<sub>2</sub>S is advantageously taken off at the bottom of the absorption stage.

10 The laden absorption liquid is then regenerated in 2 or more, advantageously from 2 to 5, preferably 2 or 3, flash stages, the final flash stage being operated under reduced pressure, and the latter being generated by means of a mechanical apparatus for producing reduced pressure

15 and a steam-jet ejector, which are connected in series, and any water losses resulting from removal of water in the gas streams taken off at the top of the absorption stage and of the flash stages may be compensated by simultaneously feeding in, at the bottom of the penultimate flash stage,

20 an amount of steam corresponding to the water loss. Preferably, a pressure of from about 0.3 to about 1, preferably from 0.4 to about 1, in particular from 0.5 to about 0.9, bar is maintained in the final flash stage. Examples of suitable mechanical apparatus for producing reduced

25 pressure are vacuum pumps and, preferably, compressors, eg. screw compressors or centrifugal compressors. The steam-jet ejector is preferably downstream of the mechanical apparatus for producing reduced pressure. In general, the flash stages are operated at from 35 to 100°C, preferably from 45 to 90°C, in particular from 55 to 85°C.

30 To compensate for water losses which arise in the process as a result of water being removed in the gas streams taken off at the top of the absorption stage and from the flash stages, an amount of steam corresponding

35 to the water loss is advantageously fed in at the bottom of the penultimate flash stage. As a rule, the water present in the gas streams taken off is substantially

removed in the form of steam. Low-pressure, medium-pressure or high-pressure steam, eg. steam under 1.5-100 bar, can be fed to the bottom of the penultimate flash stage. Preferably, low-pressure steam, eg. steam under 5 1.5-10, advantageously 1.5-5, bar, is used, since this steam is in general cheaply available.

The gas taken off at the top of the final flash stage can be released to the atmosphere or, if it still contains  $H_2S$ , can be worked up by oxidizing the  $H_2S$ , for 10 example in a Claus unit. In an advantageous embodiment of the process, the steam-jet ejector is downstream of the mechanical apparatus for producing reduced pressure, and, expediently, the gas taken off at the top of the final flash stage is fed in, together with the steam 15 used to operate the steam-jet ejector, at the bottom of the penultimate flash stage.

Where the steam used to operate the steam-jet ejector is fed in at the bottom of the penultimate flash stage, the ejector is advantageously operated using an 20 amount of steam corresponding to that required to compensate the water losses in the process. However, it is also possible to operate the steam-jet ejector with an amount of steam smaller than that required to compensate the water losses, and in addition to feed in the lacking 25 amount of steam at the bottom of the penultimate flash stage. The steam-jet ejector can be operated using medium-pressure or high-pressure steam. Medium-pressure steam, eg. under 5-20, preferably 5-10, bar, is preferably used.

30 The penultimate flash stage is advantageously operated under a pressure of about 1-30, preferably about 1-25, in particular about 1-20, bar.

Flashing is advantageously carried out using flash chambers which can, for example, also be in the form of 35 columns. These flash chambers need not contain special baffles, although columns equipped with baffles, eg. packed columns, may also be used.

The acidic gases  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$  are advantageously taken off at the top of the final flash stage or (where the gas taken off at the top of this stage is fed in, together with the steam for operating the steam-jet ejector, at the bottom of the penultimate flash stage) at the top of the penultimate flash stage. The regenerated absorption liquid taken off at the bottom of the final flash stage is recycled to the absorption stage.

The Example which follows illustrates the invention in more detail, the course of the process being shown diagrammatically in the figure.

In the figure, a gas which contains  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ , for example a natural gas containing higher hydrocarbons, eg. aliphatic  $\text{C}_2$ - $\text{C}_{10}$ -hydrocarbons, is passed under superatmospheric pressure, via line 1, into the bottom of absorption column 2. At the same time, 20-70% strength by weight aqueous methyldiethanolamine solution is passed, as an absorption liquid, via line 3 to the top of the absorption column. The absorption liquid, which is fed countercurrent to the gas, becomes laden with the acidic gases  $\text{CO}_2$  and/or  $\text{H}_2\text{S}$ , and the laden absorption liquid is taken off at the bottom of the absorption column via line 4. The washed gas is taken off at the top of the absorption column via line 11. The stream 4 of laden absorption liquid is then let down into a flash chamber 5, for example via a valve or, preferably, an expansion turbine. In this stage, a flash gas is liberated from the absorption liquid and is taken off at the top of flash chamber 5 via line 6. At the bottom of flash chamber 5, the absorption liquid which has been partially let down is taken off via line 7 and, if necessary, heated in heat exchanger 8, for example by from 0 to  $15^\circ\text{C}$ , and the absorption liquid, which may or may not have been heated, is let down into a second flash chamber 9 in which reduced pressure down to, for example, 0.3 bar is maintained by means of the mechanical apparatus 14 for producing reduced pressure, for example a compressor, and the steam-jet

ejector 13. The steam-jet ejector 13 is advantageously supplied, via line 12, with the amount of steam required to compensate the water losses of the system. The gas taken off at the top of flash chamber 9 is fed, together  
5 with the steam used for operating the steam-jet ejector 13, via line 10 to the bottom of the first flash chamber 5.

The Example which follows illustrates the invention.

#### EXAMPLE

The gas washer used comprises an absorption column  
10 and, downstream from this, three flash chambers in succession. In the absorption column, 3.15 kmol/h of a CO<sub>2</sub>-containing natural gas are washed, under 75 bar, with a 50% strength by weight aqueous methyldiethanolamine solution as the absorption liquid.

15 The gas to be treated has the following composition:

CO <sub>2</sub>	10.0 mol%
CH <sub>4</sub>	75.0 mol%
higher hydrocarbons (C <sub>2</sub> -C <sub>12</sub> -hydrocarbons)	15.0 mol%

20 The temperature of the absorption liquid in the feed to the absorption column is 70°C. The CO<sub>2</sub> content in the washed gas is less than 2 mol %. The laden wash liquid leaving the absorption column is let down to 30 bar in a first flash chamber. In this procedure, 0.011 mol/h  
25 of a hydrocarbon-rich intermediate flash gas having a CO<sub>2</sub> concentration of less than 4 mol % is liberated from the solution and taken off at the top of the first flash chamber. The partially let down absorption liquid is then heated in a heat exchanger, after which it is let down to  
30 1.5 bar in a second flash chamber. In this procedure, 0.26 kmol/h of a CO<sub>2</sub>-rich flash gas having a CO<sub>2</sub> concentration of more than 99 mol % is liberated, and removed from the top of the second flash chamber.

35 The absorption liquid taken off at the bottom of the second flash chamber is passed through a heat exchanger and then finally let down in a third flash chamber in which a pressure of 0.7 bar is maintained by means of a

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steam-jet ejector and a compressor. The gas taken off at the top of the third flash chamber is passed, together with the steam used for operating the steam-jet ejector, into the bottom of the second flash chamber. The absorption liquid  
5 taken off at the bottom of the third flash chamber is recycled to the top of the absorption column with the aid of a circulatory pump.

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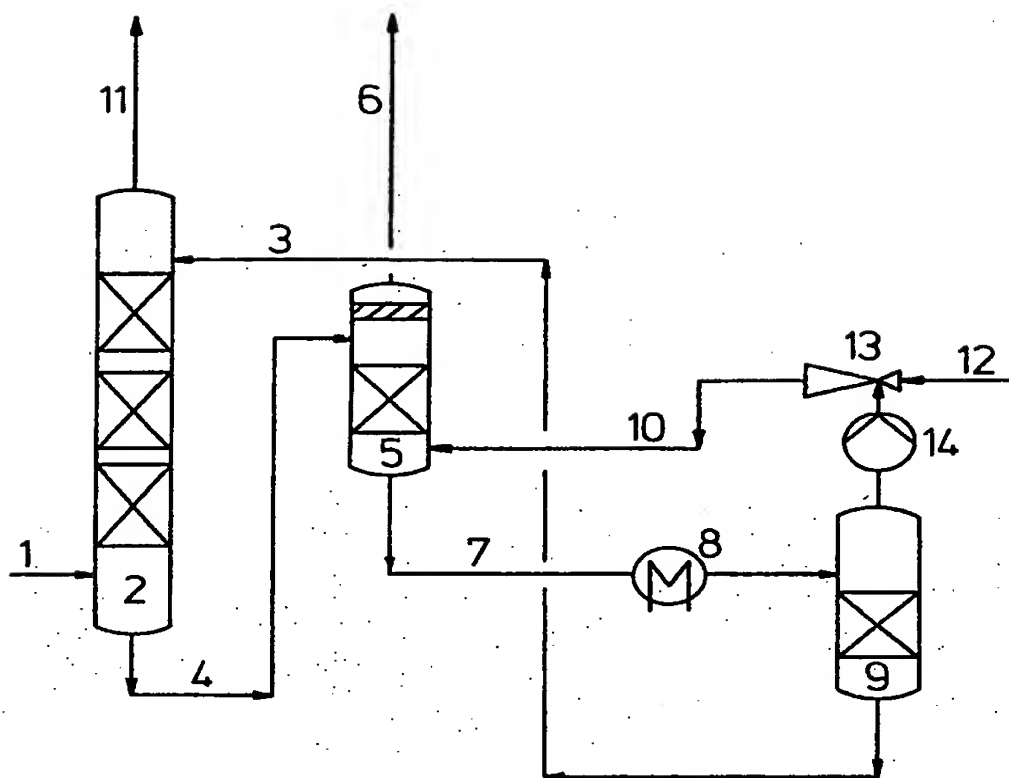
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We claim:-

1. A process for removing CO<sub>2</sub> and/or H<sub>2</sub>S from a gas containing CO<sub>2</sub> and/or H<sub>2</sub>S by means of an aqueous alkanolamine-containing absorption liquid, wherein, in an absorption stage, the gas containing CO<sub>2</sub> and/or H<sub>2</sub>S is treated at from 40 to 100°C with an aqueous absorption liquid which contains from 20 to 70% by weight of methyl-diethanolamine, the treated gas is taken off at the top of the absorption stage, the aqueous absorption liquid laden with CO<sub>2</sub> and/or H<sub>2</sub>S is removed at the bottom of this stage and is regenerated by being let down in two or more flash stages, the final flash stage being operated under reduced pressure and the latter being generated by means of a mechanical apparatus for producing reduced pressure and a steam-jet ejector, which are connected in series, and the regenerated absorption liquid is recycled to the absorption stage.
  2. A process as claimed in claim 1, wherein the steam-jet ejector is downstream of the mechanical apparatus for producing reduced pressure.
  3. A process as claimed in claim 2, wherein the gas taken off at the top of the final flash stage is fed in, together with the steam used for operating the steam-jet ejector, at the bottom of the penultimate flash stage.
- Drawing



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